Supporting Information

Polarizable Charge Equilibration Model for Transition-Metal Elements

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1. Parameter Set for PQEq3

Table S1: The electronegativity (Xo,), idempotential (Jo), shell charge *(*Qc), atomic covalent radius (R_c=R_s), and spring force constant (K_s) parameters of the PQEq3 parameter set. The units of the parameters are given in the brackets. The parameters for elements from column 4 to column 11 of the periodic table including Ti-Cu, Zr-Ag, Hf-Au are from this work. The rest of the parameters are from our previous works[1].

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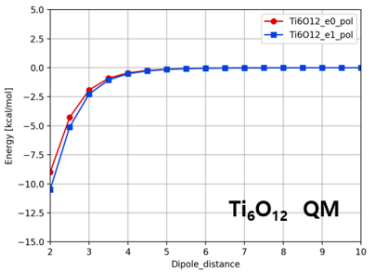
########################################
#      FORCE FIELD PARAMETERS FOR MST   #
########################################
    FFTYPE  shell
    FFVER    1.5
    NNUM          1              EL
    NTYPE         0
    NOPT          1  POLARIZABLE
    NPAR          6              Xo             Jo             Qc             Rc,s           Fcs            Qd
##########################################################
 # E  P       Xo  [eV]     Jo  [eV]   Qc  [e]     Rc  [Å]       Rs  [Å]   K2  [kcal/mol/Å2]  k4  #
##########################################################
H  1    4.72484  15.57338  1.000000    0.37100    0.37100     2037.20061           0.0
He  1    9.66000  29.84000  1.000000    1.30000    1.30000     1619.41057           0.0
Li  1    3.00600   4.77200  1.000000    1.55700    1.55700       13.64832           0.0
Be  1    4.87700   8.88600  1.000000    1.24000    1.24000       59.29709           0.0
 B  1    5.11000   9.50000  1.000000    0.82200    0.82200      109.59198           0.0
 C  1    5.50813   9.81186  1.000000    0.75900    0.75900      198.84054           0.0
 N  1    7.78778  10.80315  1.000000    0.71500    0.71500      301.87609           0.0
 O  1    8.30811  14.66128  1.000000    0.66900    0.66900      414.04451           0.0
 F  1    8.70340  17.27715  1.000000    0.70600    0.70600      596.16463           0.0
Ne  1   11.04000  21.10000  1.000000    1.76800    1.76800      842.11732           0.0
Na  1    2.84300   4.59200  1.000000    2.08500    2.08500       13.77286           0.0
Mg  1    3.95100   7.38600  1.000000    1.50000    1.50000       31.32676           0.0
Al  1    4.06000   7.18000  1.000000    1.20100    1.20100       48.83290           0.0
Si  1    4.80466   6.45956  1.000000    1.17600    1.17600       60.04769           0.0
 P  1    6.52204   7.13703  1.000000    1.10200    1.10200       91.47760           0.0
 S  1    8.19185   8.64528  1.000000    1.04700    1.04700      114.50472           0.0
```

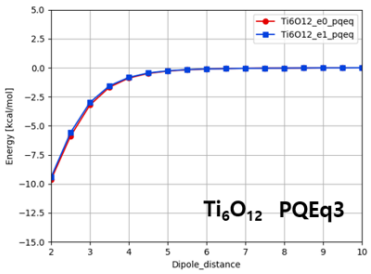
Cl	1	8.20651	9.73890	1.000000	0.99400	0.99400	152.32280	0.0
Ar	1	9.46500	12.71000	1.000000	2.10800	2.10800	202.34215	0.0
K	1	2.42100	3.84000	1.000000	2.58600	2.58600	7.71165	0.0
Ca	1	3.23100	5.76000	1.000000	2.00000	2.00000	14.56420	0.0
Sc	1	3.39500	6.16000	1.000000	1.75000	1.75000	18.65526	0.0
Ti	1	3.45760	6.74120	1.000000	0.79300	0.79300	209.00000	0.0
V	1	3.63609	6.22019	1.000000	0.80100	0.80100	268.00000	0.0
Cr	1	3.72117	6.09068	1.000000	0.82900	0.82900	286.00000	0.0
Mn	1	3.21702	8.43404	1.000000	0.36100	0.36100	409.00000	0.0
Fe	1	4.02785	7.74923	1.000000	0.58300	0.58300	404.00000	0.0
Co	1	4.27163	7.21875	1.000000	0.65000	0.65000	542.00000	0.0
Ni	1	4.39852	6.48272	1.000000	0.80500	0.80500	488.00000	0.0
Cu	1	4.48109	6.49059	1.000000	0.77900	0.77900	536.00000	0.0
Zn	1	5.10600	8.57000	1.000000	1.40000	1.40000	57.75021	0.0
Ga	1	3.64100	6.32000	1.000000	1.21100	1.21100	40.89454	0.0
Ge	1	4.80386	6.71243	1.000000	1.18900	1.18900	56.86022	0.0
As	1	5.41473	7.58310	1.000000	1.20400	1.20400	77.04494	0.0
Se	1	6.05692	8.40969	1.000000	1.22400	1.22400	88.08056	0.0
Br	1	7.79000	8.79002	1.000000	1.14100	1.14100	108.87334	0.0
Kr	1	8.50500	11.43000	1.000000	2.27000	2.27000	133.65952	0.0
Rb	1	2.33100	3.69200	1.000000	2.77000	2.77000	7.02929	0.0
Sr	1	3.02400	4.88000	1.000000	2.41500	2.41500	12.03129	0.0
Y	1	3.83000	5.62000	1.000000	1.99800	1.99800	14.62836	0.0
Zr	1	3.53045	6.20690	1.000000	0.82700	0.82700	193.00000	0.0
Nb	1	3.82642	5.86485	1.000000	0.84000	0.84000	247.00000	0.0
Mo	1	3.92092	6.34301	1.000000	0.75100	0.75100	259.00000	0.0
Tc	1	3.88869	6.46138	1.000000	0.72600	0.72600	239.00000	0.0
Ru	1	4.20344	6.31412	1.000000	0.75000	0.75000	346.00000	0.0
Rh	1	4.30089	6.31601	1.000000	0.72900	0.72900	386.00000	0.0
Pd	1	4.44950	7.77472	1.000000	0.55900	0.55900	438.00000	0.0
Ag	1	4.44036	6.27175	1.000000	0.74500	0.74500	666.00000	0.0
Cd	1	5.03400	7.91400	1.000000	1.60000	1.60000	45.11735	0.0
In	1	3.50600	5.79200	1.000000	1.40400	1.40400	32.55526	0.0

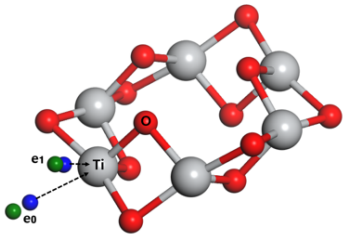
Sn	1	4.62392	6.45025	1.000000	1.35400	1.35400	52.87639	0.0
Sb	1	4.56949	6.45124	1.000000	1.40400	1.40400	50.31268	0.0
Te	1	6.02877	6.80311	1.000000	1.38000	1.38000	60.37522	0.0
I	1	6.15480	7.50909	1.000000	1.33300	1.33300	62.06798	0.0
Xe	1	7.59500	9.95000	1.000000	2.45900	2.45900	82.11269	0.0
Cs	1	2.18300	3.42200	1.000000	2.98400	2.98400	5.58842	0.0
Ba	1	2.81400	4.79200	1.000000	2.44200	2.44200	8.36432	0.0
La	1	2.83550	5.48300	1.000000	2.07100	2.07100	10.67729	0.0
Ce	1	2.77400	5.38400	1.000000	1.92500	1.92500	11.21837	0.0
Pr	1	2.85800	5.12800	1.000000	2.00700	2.00700	11.77531	0.0
Nd	1	2.86850	5.24100	1.000000	2.00700	2.00700	10.57528	0.0
Pm	1	2.88100	5.34600	1.000000	2.00000	2.00000	11.03202	0.0
Sm	1	2.91150	5.43900	1.000000	1.97800	1.97800	11.52999	0.0
Eu	1	2.87850	5.57500	1.000000	2.22700	2.22700	11.98786	0.0
Gd	1	3.16650	5.94900	1.000000	1.96800	1.96800	14.13037	0.0
Tb	1	3.01800	5.66800	1.000000	1.95400	1.95400	13.02211	0.0
Dy	1	3.05550	5.74300	1.000000	1.93400	1.93400	13.55362	0.0
Ho	1	3.12700	5.78200	1.000000	1.92500	1.92500	14.07050	0.0
Er	1	3.18650	5.82900	1.000000	1.91500	1.91500	14.62836	0.0
Tm	1	3.25140	5.86580	1.000000	2.00000	2.00000	15.23228	0.0
Yb	1	3.28890	5.93000	1.000000	2.15800	2.15800	15.88822	0.0
Lu	1	2.96290	4.92580	1.000000	1.89600	1.89600	15.16273	0.0
Hf	1	3.41253	6.82507	1.000000	0.73200	0.73200	210.00000	0.0
Ta	1	3.93629	7.22657	1.000000	0.64100	0.64100	305.00000	0.0
W	1	4.34014	7.04777	1.000000	0.65500	0.65500	385.00000	0.0
Re	1	3.94726	7.77252	1.000000	0.57500	0.57500	342.00000	0.0
Os	1	4.75802	7.36041	1.000000	0.58900	0.58900	391.00000	0.0
Ir	1	5.26569	7.40266	1.000000	0.50800	0.50800	340.00000	0.0
Pt	1	5.54197	6.83373	1.000000	0.69700	0.69700	511.00000	0.0
Au	1	5.76708	6.91695	1.000000	0.55600	0.55600	740.00000	0.0
Hg	1	6.27000	8.32000	1.000000	1.60000	1.60000	66.14815	0.0
Tl	1	3.20000	5.80000	1.000000	1.53000	1.53000	43.69259	0.0
Pb	1	3.90000	7.06000	1.000000	1.44400	1.44400	47.57360	0.0

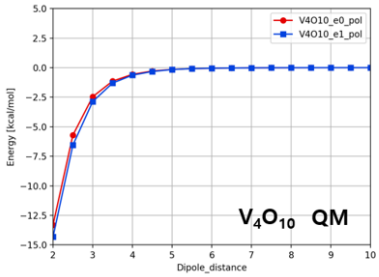
Bi	1	4.53181	7.32783	1.000000	1.51400	1.51400	44.87347	0.0
Po	1	4.42943	8.40996	1.000000	1.48000	1.48000	48.83290	0.0
At	1	4.53674	8.99576	1.000000	1.47000	1.47000	55.34395	0.0
Rn	1	5.37000	10.74000	1.000000	2.20000	2.20000	62.65353	0.0
Fr	1	2.00000	4.00000	1.000000	2.30000	2.30000	6.83259	0.0
Ra	1	2.84300	4.86800	1.000000	2.20000	2.20000	8.67007	0.0
Ac	1	2.83500	5.67000	1.000000	2.10800	2.10800	10.34466	0.0
Th	1	3.17500	5.81000	1.000000	2.01800	2.01800	10.34466	0.0
Pa	1	2.98500	5.81000	1.000000	1.80000	1.80000	13.07337	0.0
U	1	3.34100	5.70600	1.000000	1.71300	1.71300	13.33589	0.0
Np	1	3.54900	5.43400	1.000000	1.80000	1.80000	13.38967	0.0
Pu	1	3.24300	5.63800	1.000000	1.84000	1.84000	13.55362	0.0
Am	1	2.98950	6.00700	1.000000	1.94200	1.94200	14.25166	0.0
Cm	1	2.83150	6.37900	1.000000	1.90000	1.90000	14.43755	0.0
Bk	1	3.19350	6.07100	1.000000	1.90000	1.90000	14.62836	0.0
Cf	1	3.19700	6.20200	1.000000	1.90000	1.90000	16.19823	0.0
Es	1	3.33300	6.17800	1.000000	1.90000	1.90000	16.85603	0.0
Fm	1	3.40000	6.20000	1.000000	1.90000	1.90000	13.95226	0.0
Md	1	3.47000	6.22000	1.000000	1.90000	1.90000	18.24526	0.0
No	1	3.47500	6.35000	1.000000	1.90000	1.90000	20.24779	0.0
Lr	0	3.50000	6.40000	1.000000	1.90000	1.90000	0.00000	0.0

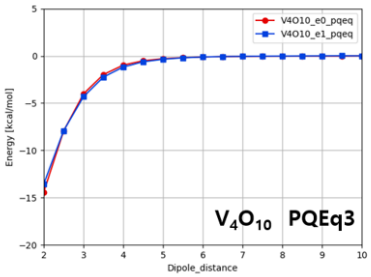
2. Net Interaction Energy Curves

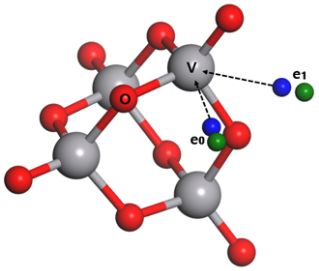


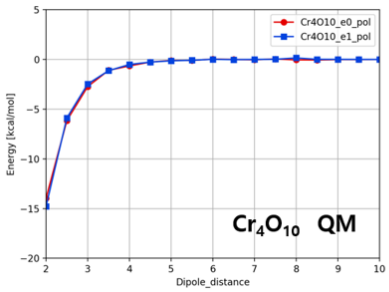


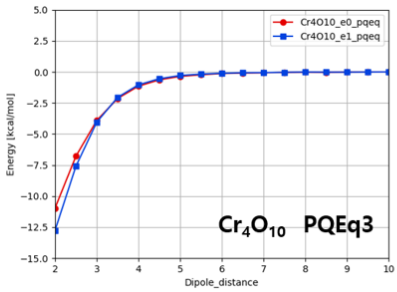


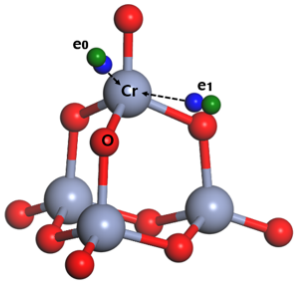


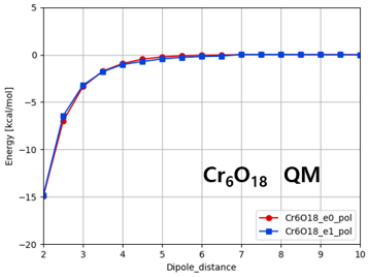


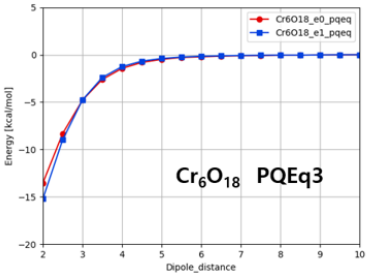


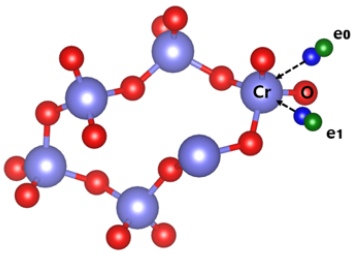


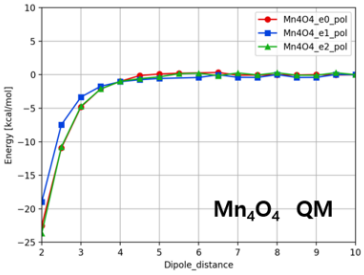




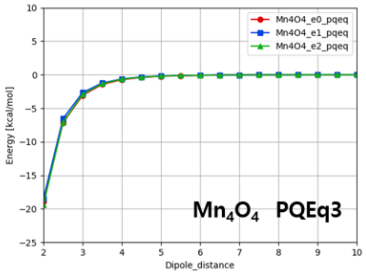




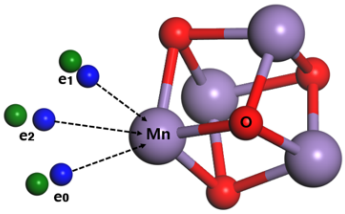


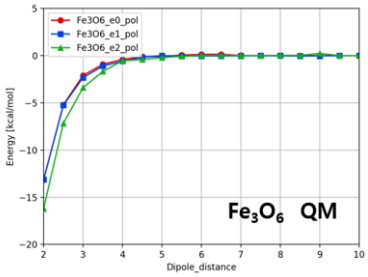


Mn_4O_4 QM



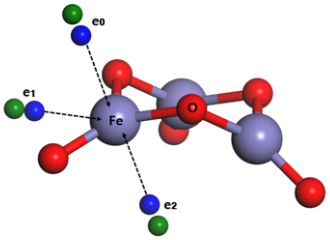
Mn_4O_4 PQEq3

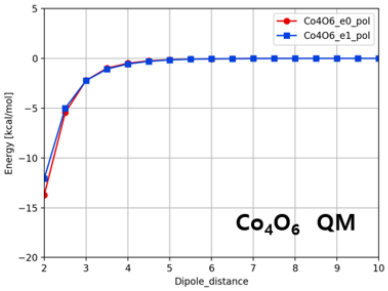




Fe_3O_6 QM

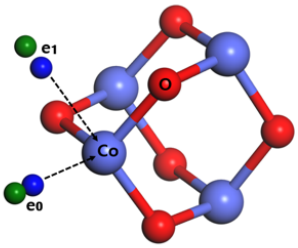
Fe_3O_6 PQEq3

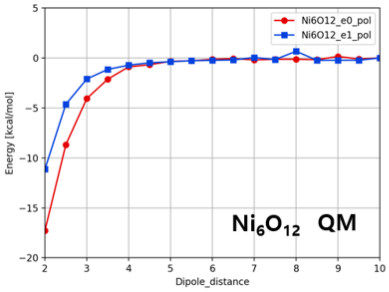




Co_4O_6 QM

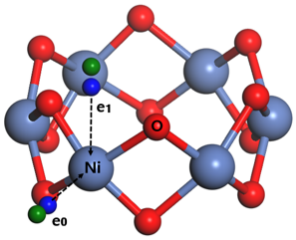
Co_4O_6 PQEq3

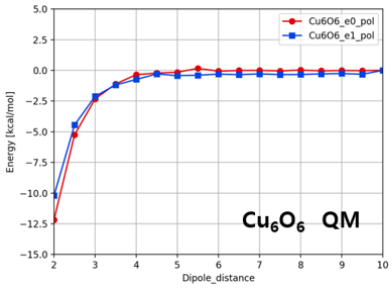


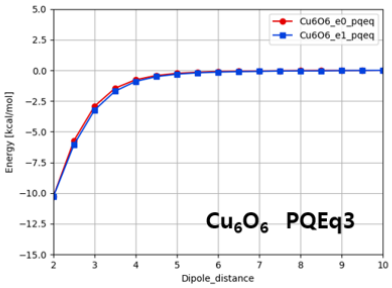


Ni_6O_{12} QM

Ni_6O_{12} PQEq3




Cu6O6_e0_pol
Cu6O6_e1_pol
Energy [kcal/mol]
Dipole_distance
Cu6O6 QM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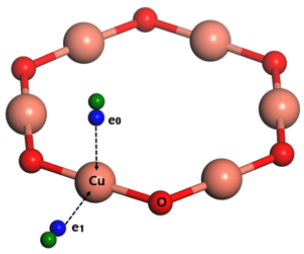
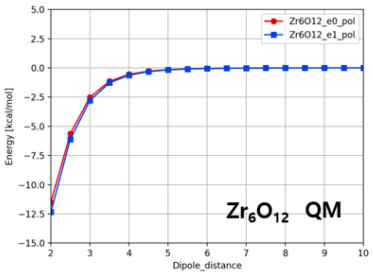
Cu6O6_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Cu6O6 PQEq3


e0
Cu
O
e1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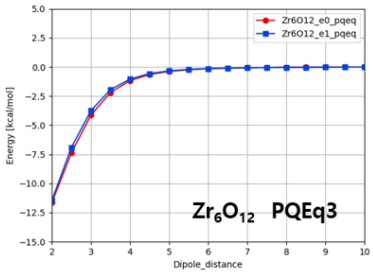
Zr6O12_e1_pol
Energy [kcal/mol]
Dipole_distance
Zr6O12 QM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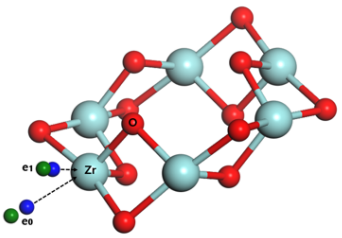
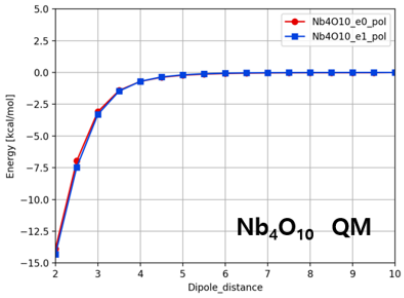
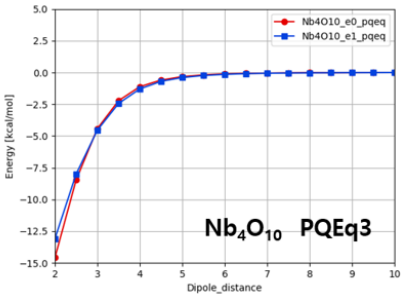
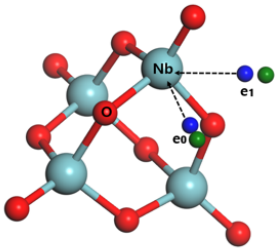
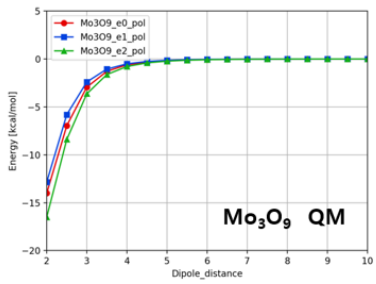
Zr6O12_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Zr6O12 PQEq3

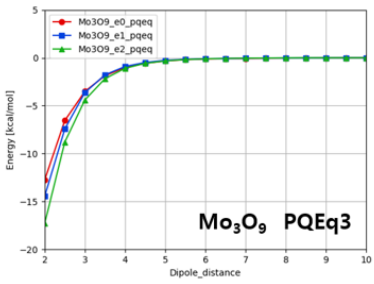

O
e1
Zr
e0

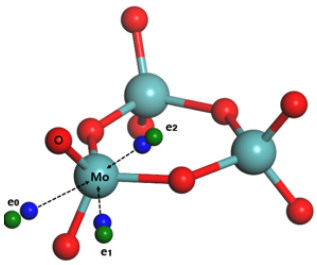

Nb4O10_e0_pol
Nb4O10_e1_pol
Energy [kcal/mol]
Dipole_distance
Nb4O10 QM

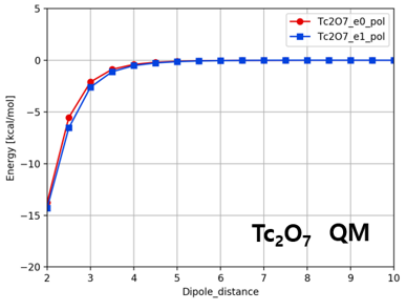

Nb4O10_e0_pqeq
Nb4O10_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Nb4O10 PQEq3

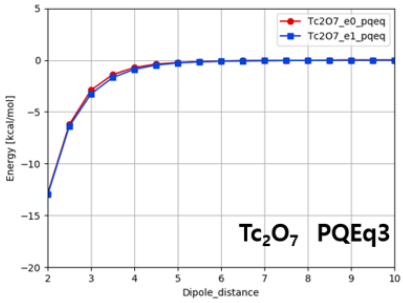

Nb
e1
O
e0

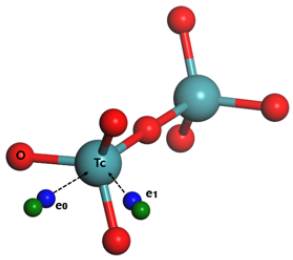

Mo3O9_e0_pol
Mo3O9_e1_pol
Mo3O9_e2_pol
Energy [kcal/mol]
Dipole_distance
Mo3O9 QM

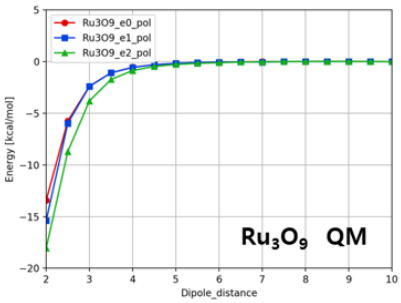

Mo3O9_e0_pqeq
Mo3O9_e1_pqeq
Mo3O9_e2_pqeq
Energy [kcal/mol]
Dipole_distance
Mo3O9 PQEq3

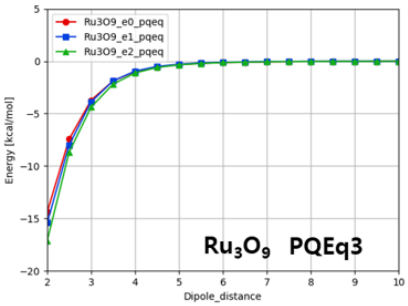

e2
O
Mo
e0
e1

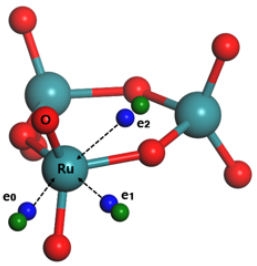

Tc2O7_e0_pol
Tc2O7_e1_pol
Energy [kcal/mol]
Dipole_distance
Tc2O7 QM

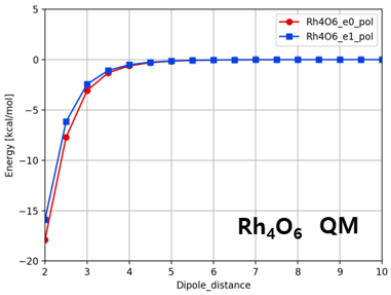

Tc2O7_e0_pqeq
Tc2O7_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Tc2O7 PQEq3

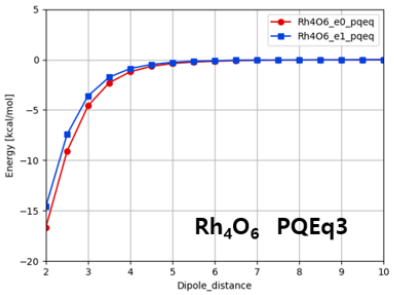

O
Tc
e0
e1

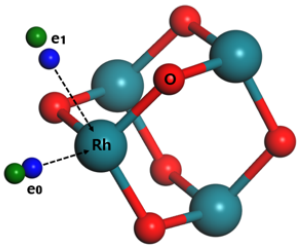

Ru3O9_e0_pol
Ru3O9_e1_pol
Ru3O9_e2_pol
Energy [kcal/mol]
Dipole_distance
Ru3O9 QM

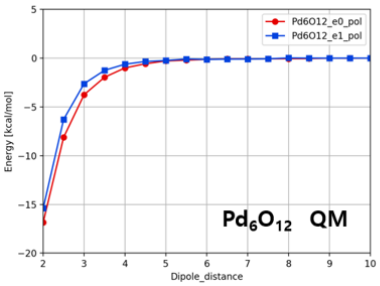

Ru3O9_e0_pqeq
Ru3O9_e1_pqeq
Ru3O9_e2_pqeq
Energy [kcal/mol]
Dipole_distance
Ru3O9 PQEq3

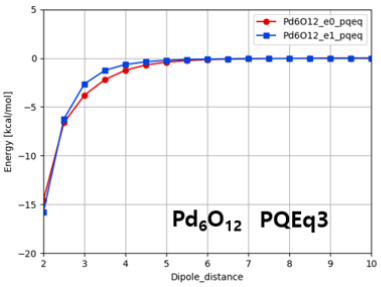

O
e2
Ru
e0
e1

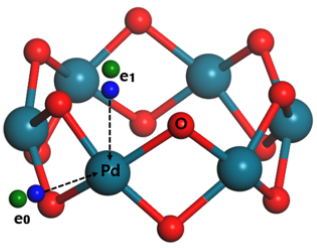

Rh4O6_e0_pol
Rh4O6_e1_pol
Energy [kcal/mol]
Dipole_distance
Rh4O6 QM

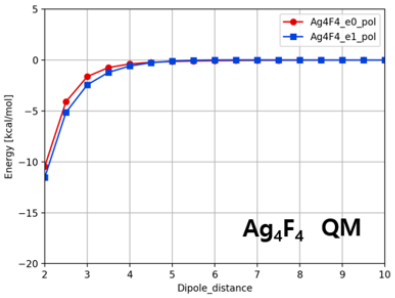

Rh4O6_e0_pqeq
Rh4O6_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Rh4O6 PQEq3

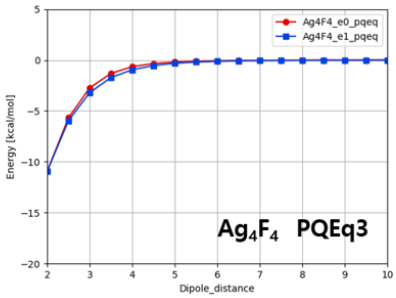

e1
O
Rh
e0

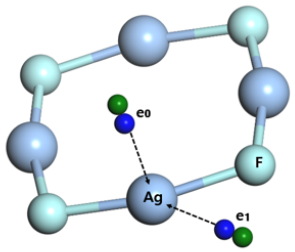

Pd6O12_e0_pol
Pd6O12_e1_pol
Energy [kcal/mol]
Dipole_distance
Pd6O12 QM

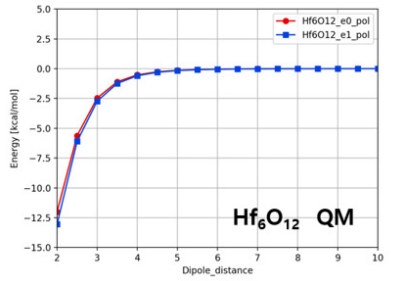

Pd6O12_e0_pqeq
Pd6O12_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Pd6O12 PQEq3

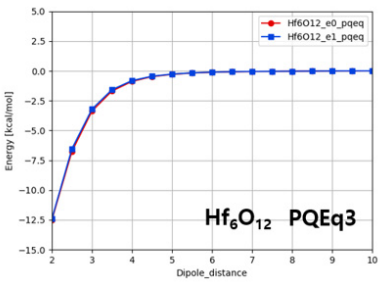

e1
O
Pd
e0

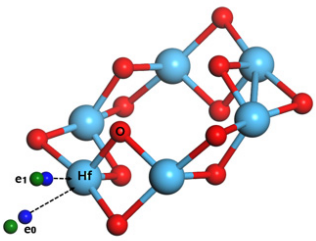

Ag4F4_e0_pol
Ag4F4_e1_pol
Energy [kcal/mol]
Dipole_distance
Ag4F4 QM

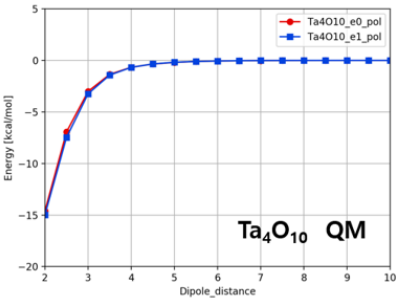

Ag4F4_e0_pqeq
Ag4F4_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Ag4F4 PQEq3

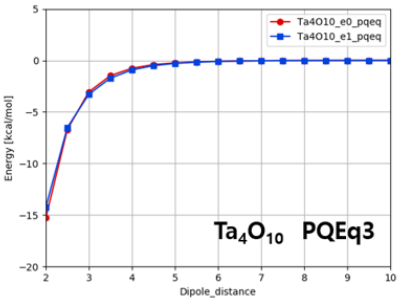

e0
F
Ag
e1

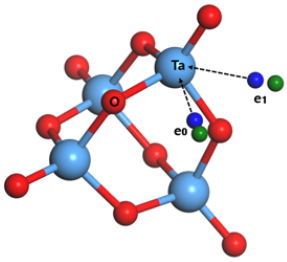

Hf6O12_e0_pol
Hf6O12_e1_pol
Energy [kcal/mol]
Dipole_distance
Hf6O12 QM

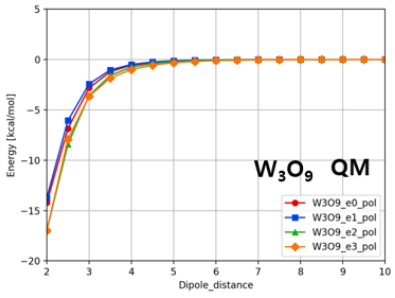

Hf6O12_e0_pqeq
Hf6O12_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Hf6O12 PQEq3

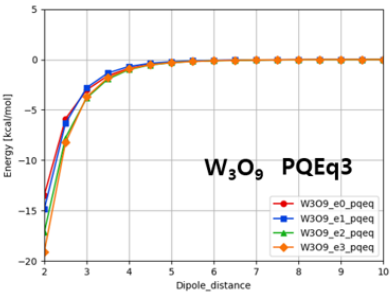

O
e1
Hf
e0

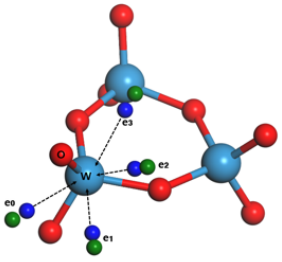

Ta4O10_e0_pol
Ta4O10_e1_pol
Energy [kcal/mol]
Dipole_distance
Ta4O10 QM

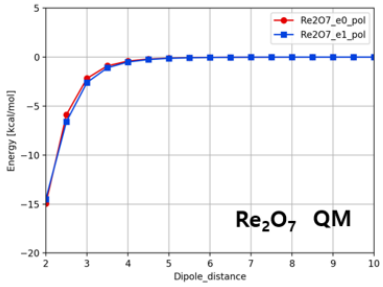

Ta4O10_e0_pqeq
Ta4O10_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Ta4O10 PQEq3

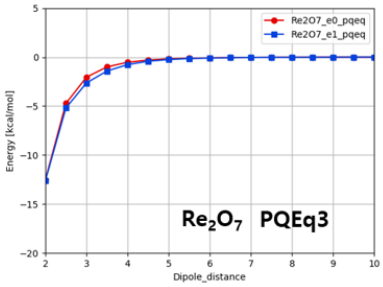

Ta
e1
O
e0

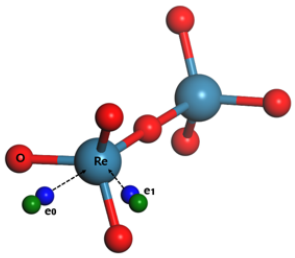

W3O9_e0_pol
W3O9_e1_pol
W3O9_e2_pol
W3O9_e3_pol
Energy [kcal/mol]
Dipole_distance
W3O9 QM

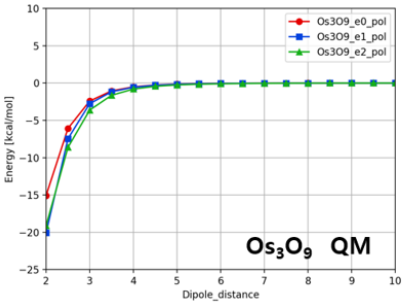

W3O9_e0_pqeq
W3O9_e1_pqeq
W3O9_e2_pqeq
W3O9_e3_pqeq
Energy [kcal/mol]
Dipole_distance
W3O9 PQEq3

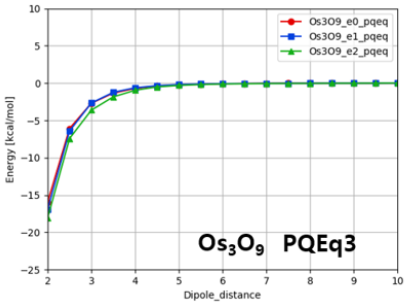

e3
O
e2
W
e0
e1

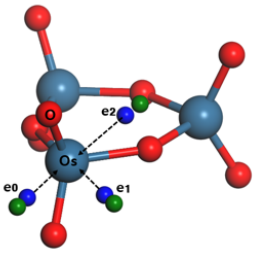

Re2O7_e0_pol
Re2O7_e1_pol
Energy [kcal/mol]
Dipole_distance
Re2O7 QM

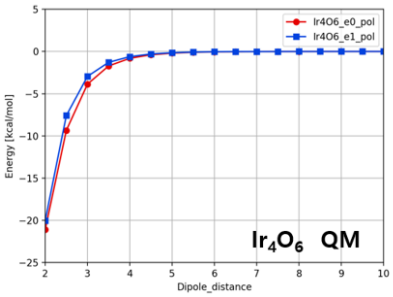

Re2O7_e0_pqeq
Re2O7_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Re2O7 PQEq3

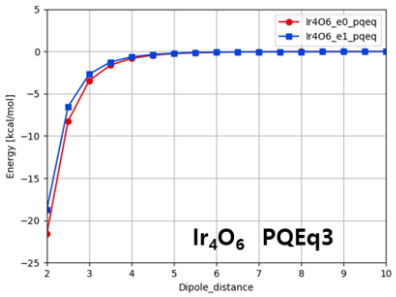

O
Re
e1
e0

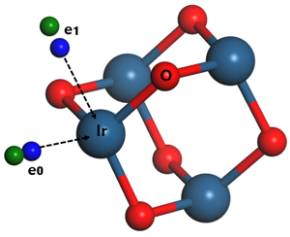

Os3O9_e0_pol
Os3O9_e1_pol
Os3O9_e2_pol
Energy [kcal/mol]
Dipole_distance
Os3O9 QM

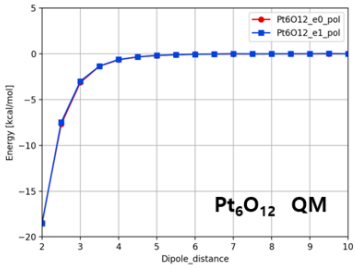

Os3O9_e0_pqeq
Os3O9_e1_pqeq
Os3O9_e2_pqeq
Energy [kcal/mol]
Dipole_distance
Os3O9 PQEq3

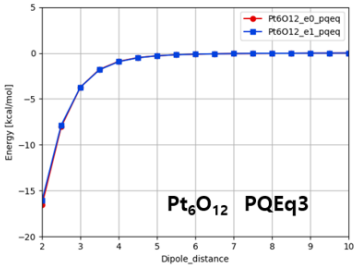

O
e2
Os
e0
e1

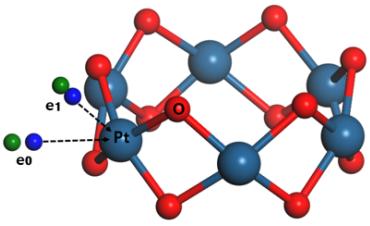

Ir4O6_e0_pol
Ir4O6_e1_pol
Energy [kcal/mol]
Dipole_distance
Ir4O6 QM


Ir4O6_e0_pqeq
Ir4O6_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Ir4O6 PQEq3


e1
O
Ir
e0


Pt6O12_e0_pol
Pt6O12_e1_pol
Energy [kcal/mol]
Dipole_distance
Pt6O12 QM


Pt6O12_e0_pqeq
Pt6O12_e1_pqeq
Energy [kcal/mol]
Dipole_distance
Pt6O12 PQEq3


e1
O
Pt
e0

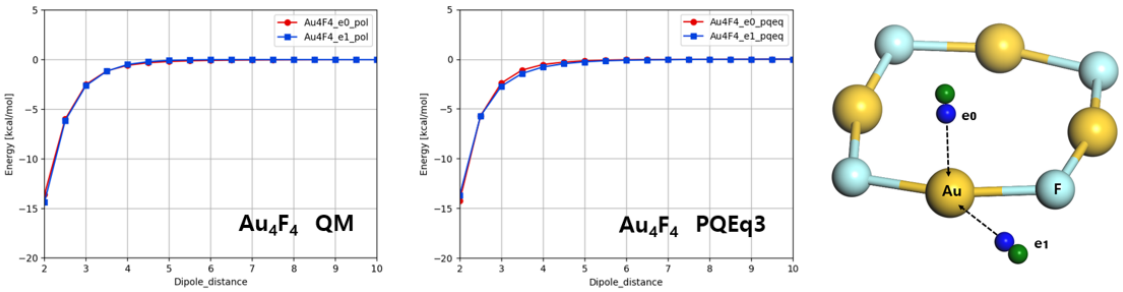
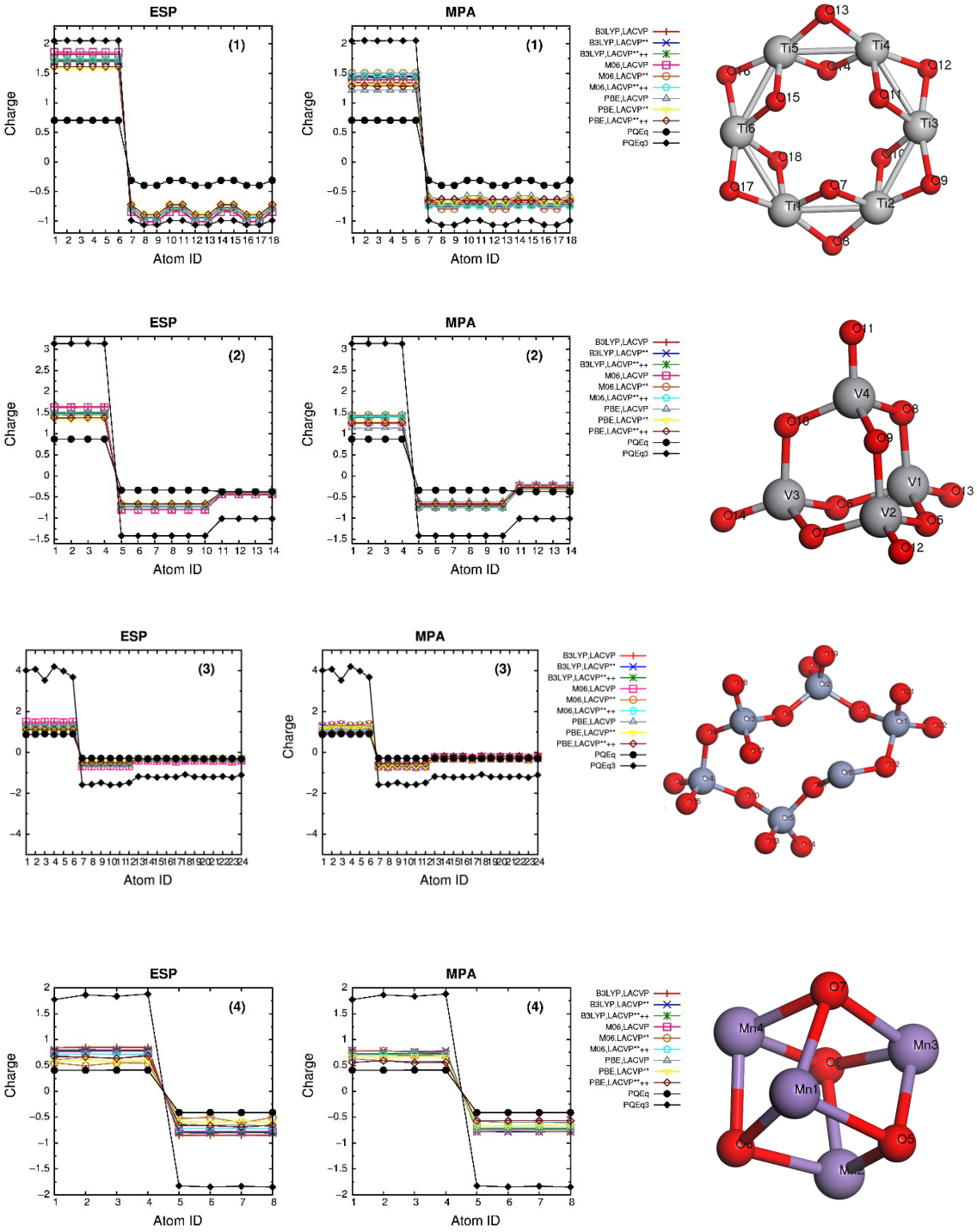
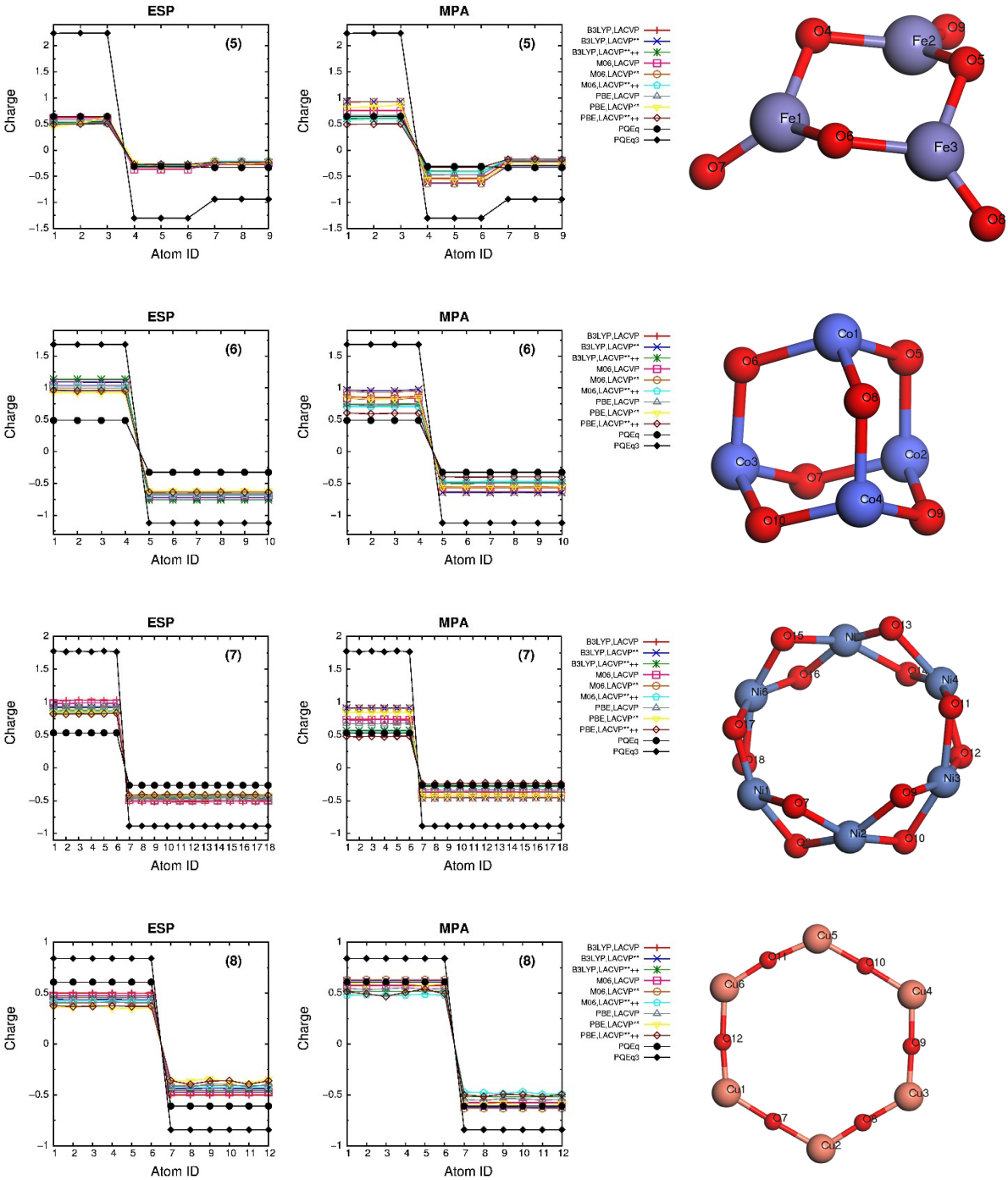


Figure S1: A comparison between QM (B3LYP with LACVP**) with PQEq3 via the net interaction energies. Molecular configurations are depicted on the right side for each polarization energy plot to describe the direction of the dipole scan.

3. Charge Comparison between PQEq, PQEq3, and QM




ESP
MPA
(5)
(6)
(7)
(8)
Charge
Atom ID
B3LYP,LACVP
B3LYP,LACVP**
B3LYP,LACVP**++
M06,LACVP
M06,LACVP**
M06,LACVP**++
PBE,LACVP
PBE,LACVP**
PBE,LACVP**++
PQEq
PQEq3
O4
Fe2
O9
O5
Fe1
O6
Fe3
O7
O8
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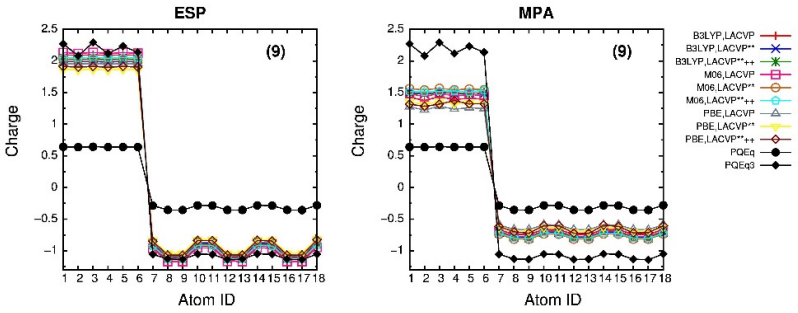
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PQEq3
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Zr4
O14
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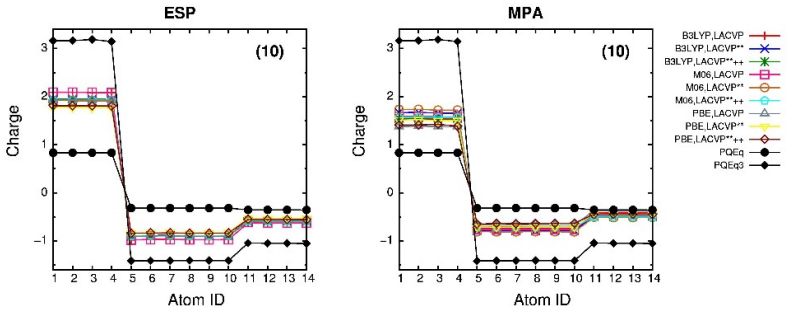
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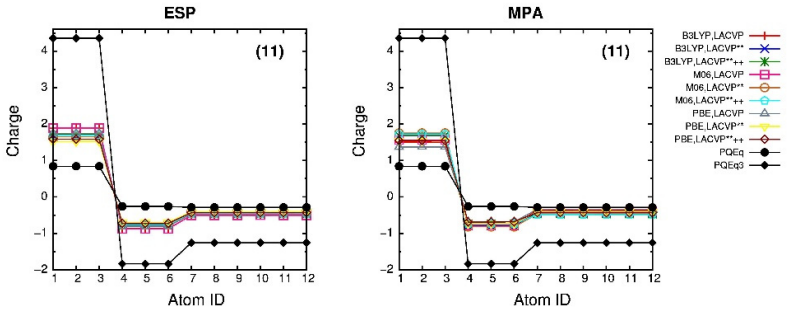
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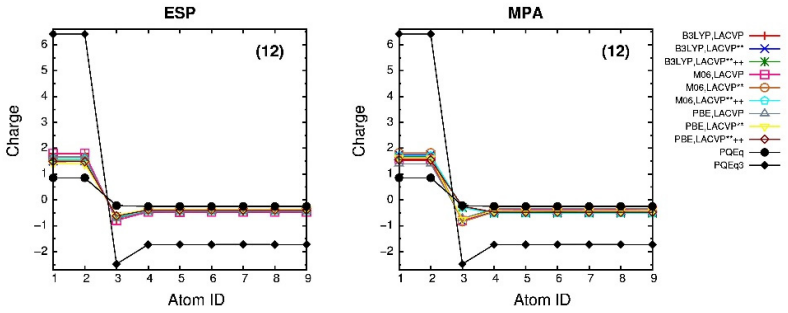
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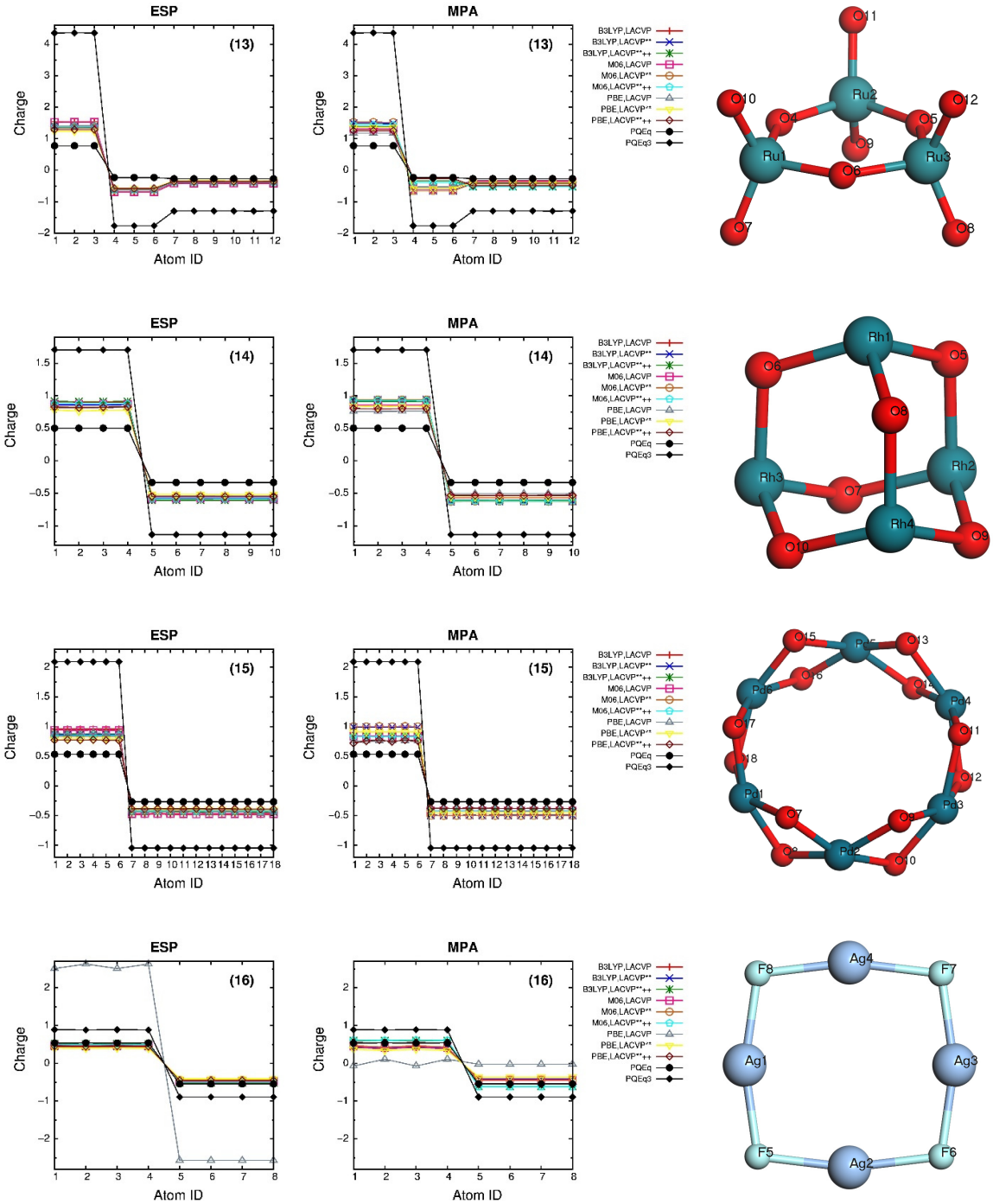
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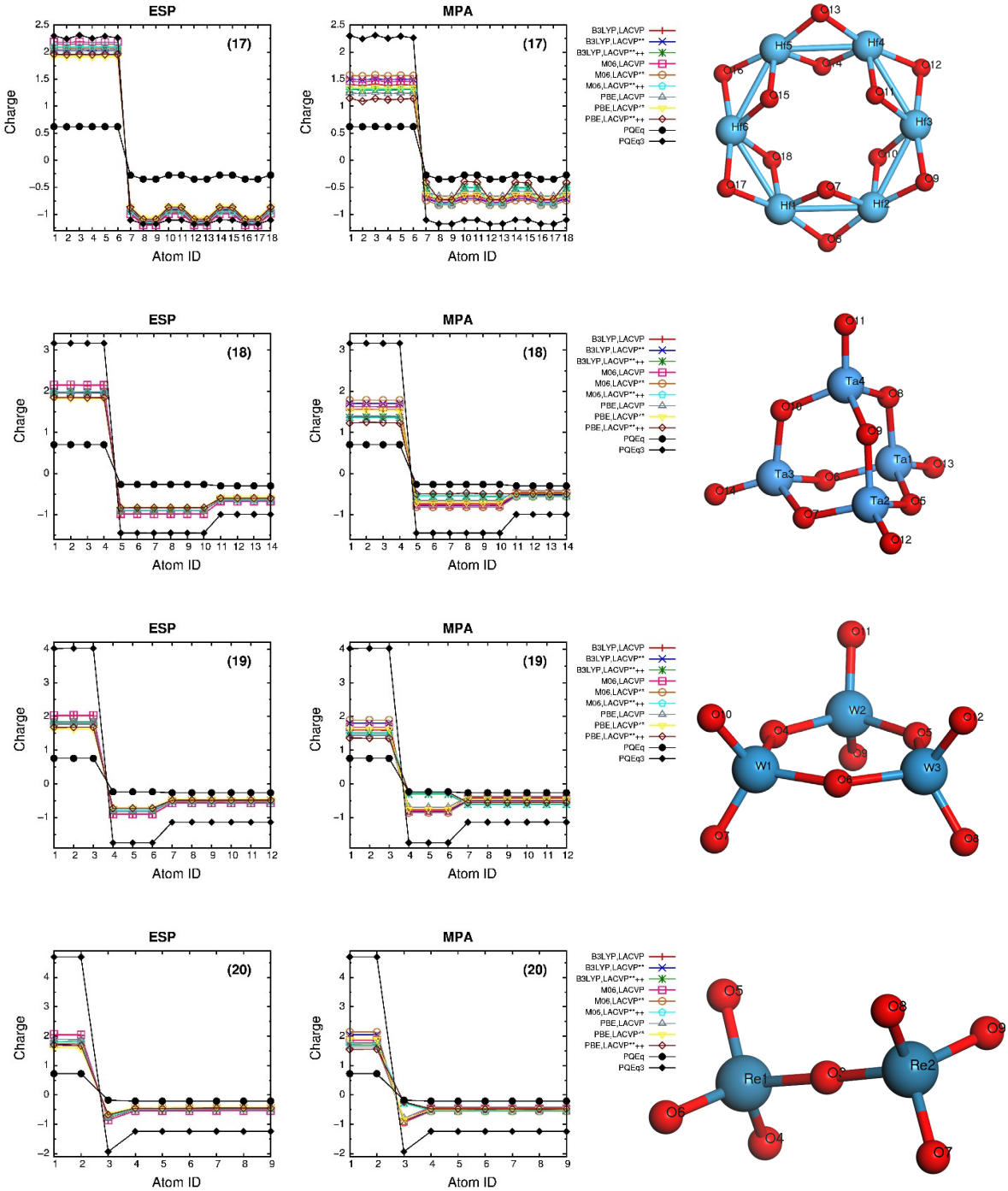
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PQEq3
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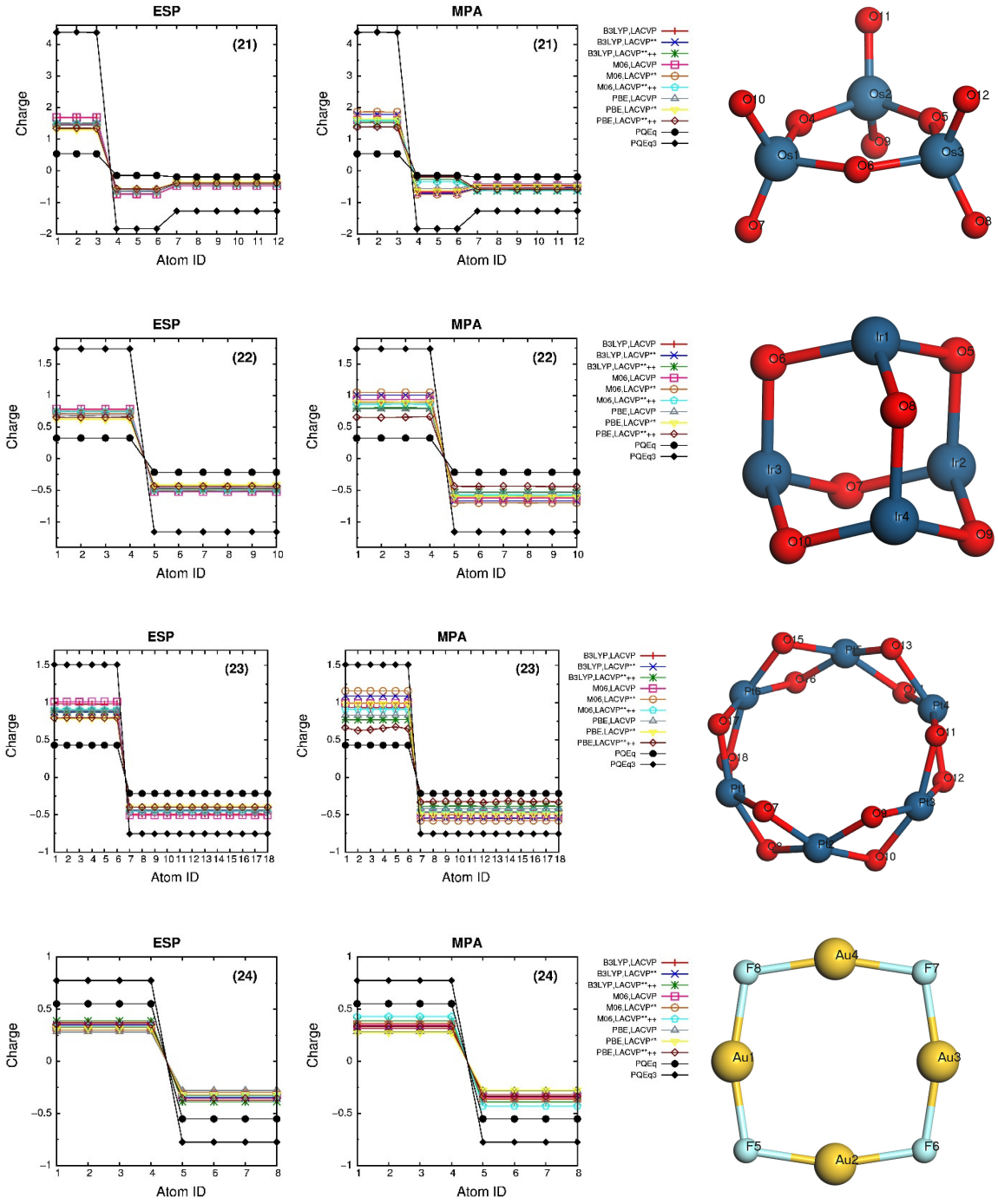

Figure S2: A comparison of the partial charge calculations using electrostatic potentials (ESP) and Mulliken population analysis (MPA) with PQEq, PQEq3, and combinations of B3LYP, M06, PBE with LACVP, LACVP++, and LACVP++**.

4. Comparison between $PQEq_0$, and PQEq3 for oxygen element

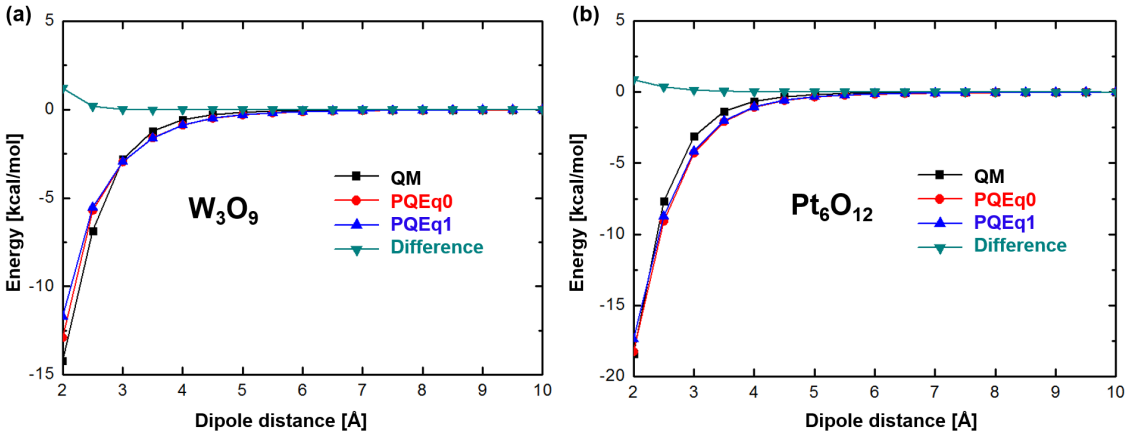

Figure S3: A comparison between PQEq0 and PQEq1 for Oxygen for (a) W_3O_9 and (b) Pt_6O_{12}. The change in χ and J for oxygen shows negligible differences.

5. Comparison of atomic radius between experimental and PQEq3 values

Table S2: The experimental *R* values are estimated by averaging over the values taken from literature for the same oxidation states (with different coordination numbers) that were used in our oxide cluster models. For the case that there is no corresponding experimental values, we averaged out the atomic radius for ions with one extra charge and one less charge.

Element	Exp.	PQEq3	Element	Exp.	PQEq3
Ti	0.59	0.793	Ru	0.48	0.75
V	0.45	0.801	Rh	0.67	0.729
Cr	0.42	0.829	Pd	0.62	0.559
Mn	0.58	0.361	Ag	0.87	0.745
Fe	0.61	0.583	Hf	0.71	0.732
Co	0.55	0.65	Ta	0.64	0.641
Ni	0.56	0.805	W	0.51	0.655
Cu	0.65	0.779	Re	0.46	0.575
Zr	0.76	0.827	Os	0.55	0.589
Nb	0.62	0.84	Ir	0.68	0.508
Mo	0.58	0.751	Pt	0.63	0.697
Tc	0.65	0.726	Au	0.95	0.556

6. Comparison of R and Ks values before and after optimization

Table S3: The atomic covalent radius R_c=R_s, and spring force constant K_s for original PQEq and PQEq3 for TMs.

Atom	PQEq0		PQEq3	
	R_c=R_s (Å)	K_s (kcal/mol/Å^2)	R_c=R_s (Å)	K_s (kcal/mol/Å^2)
Ti	1.607	22.7	0.793	209
V	1.47	26.8	0.801	268
Cr	1.402	28.6	0.829	286
Mn	1.533	35.3	0.361	409
Fe	1.393	39.5	0.583	404
Co	1.406	44.3	0.65	542
Ni	1.398	48.8	0.805	488
Cu	1.434	53.6	0.779	537
Zr	1.758	18.6	0.827	193
Nb	1.603	21.2	0.84	247
Mo	1.53	25.9	0.751	259
Tc	1.5	29.1	0.726	239
Ru	1.5	34.6	0.75	346
Rh	1.509	38.6	0.729	386
Pd	1.544	69.2	0.559	438
Ag	1.622	49.0	0.745	666
Hf	1.759	20.5	0.732	210
Ta	1.605	25.3	0.641	305
W	1.538	29.9	0.655	385
Re	1.6	34.2	0.575	342
Os	1.7	39.1	0.589	391
Ir	1.866	43.7	0.508	437
Pt	1.557	51.1	0.697	511
Au	1.618	57.3	0.556	740

7. Effects of diffuse functionals on electric dipole polarization

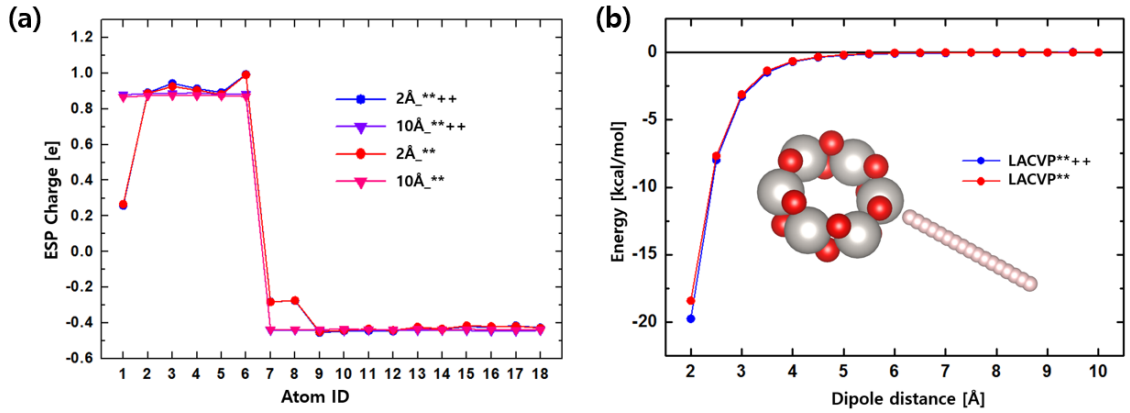

Figure S4: A comparison between diffuse functionals(++) for B3LYP/LACVP** for Pt_6O_{12} cluster: (a) ESP charge distribution and (b) electric dipole scan towards the cluster. The charge distribution and polarization energy negligibly change on addition of diffuse function.

8. Dielectric response and polarization scalability of PQEq model

To check if there is any metallic scalability problem[2] in PQEq model, we computed the dielectric constant of polyethylene (PE) as a function of chain length in the presence of an external electric field.

We applied a constant electric field, E_0, in the z direction, along the backbone of the polymer (see Figure S5). The number of C_2H_4 monomer units (N) was increased from 1 to 15 units along the backbone chain. The effect of E_0 was included in the charge and shell position calculations. Here,

$$F_{inter} = -\frac{\partial}{\partial r_{is}}\left\{\sum_{ia>ib} T(r_{ia,jb}) C_{ia,jb}(r_{ia,jb}) q_{ia} q_{jb}\right\} + \sum_a r_{ia} \mathrm{E}_0 \tag{1}$$

$$F_{intra} = -\frac{\partial}{\partial r_{is}}\left(\frac{1}{2} K_s r_{ic,is}^2\right) \tag{2}$$

where $r_{ia,jb}$ [i, j = 1,…, N; a, b = core(c) or shell(s)] are charge-charge distances. See the text for the description of other parameters. We solve $F_{inter} = F_{intra}$ to determine r_{is} using the Newton-Raphson method. The charges were updated using the preconditioned-conjugate-gradient (PCG) method as described in the text. The polarization density (P) is computed by

$$P = \sum_{ia} q_{is}(r_{ia} - r_{ia}^0) \tag{3}$$

where r_{ia}^0 is the charge position in the absence of external electric field E_0. Finally, the dielectric constant is computed by,

$$\mathcal{E} = 1 + \frac{P}{V \epsilon_0 E_0} \tag{4}$$

where V is volume and ε_0 is the vacuum permittivity.

The change of $\mathcal{E}$ versus the number of C_2H_4 units (N) for a constant field along z direction (E_0=1.0 V/Å) is shown in Figure S5. Here, we see that $\mathcal{E}$ decreases with N for N<6 reaching a constant value for N>10. These result show that PQEq does not have the metallic scaling problem postulated by the reviewer. Thus PQEq is capable of correctly describing dielectric response.

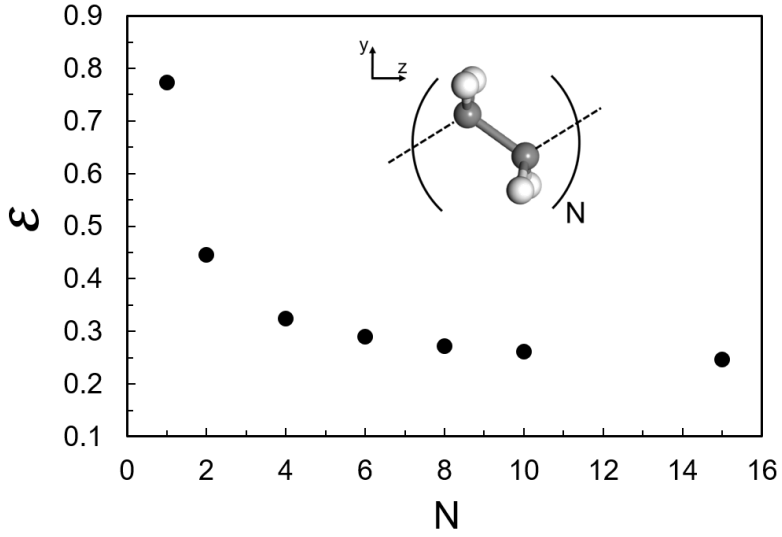

Figure S5. The change of dielectric constant, ε, as a function of the number of polyethylene monomer units (N) in the presence of an external electric field (E_0=1.0 V/Å) in the z direction.

References:

1. (a) Naserifar, S.; Brooks, D. J.; Goddard III, W. A.; Cvicek, V., Polarizable charge equilibration model for predicting accurate electrostatic interactions in molecules and solids. *J. Chem. Phys.* **2017,** *146*, 124117; (b) Oppenheim, J. J.; Naserifar, S.; Goddard III, W. A., Extension of the Polarizable Charge Equilibration Model to Higher Oxidation States with Applications to Ge, As, Se, Br, Sn, Sb, Te, I, Pb, Bi, Po, and At Elements. *J. Phys. Chem. A* **2018,** *122*, 639-645.
2. Lee Warren, G.; Davis, J. E.; Patel, S., Origin and control of superlinear polarizability scaling in chemical potential equalization methods. *J. Chem. Phys.* **2008,** *128*, 144110.